# Stepwise Self-Assembly monolayer of Sodium Oleate on (111) Fluorite: Insights from Molecular Dynamics Simulations

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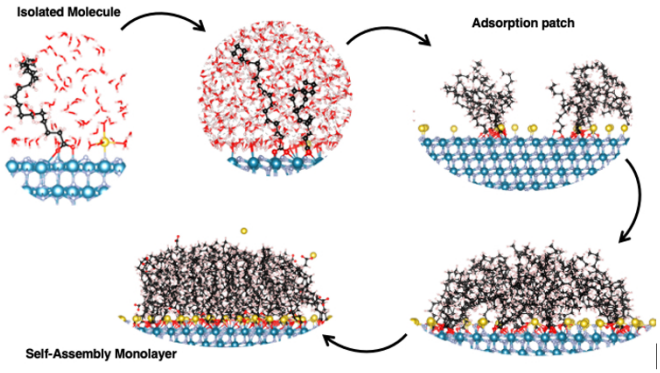
Fluorite ($CaF_2$), the main natural source of hydrofluoric acid, is commonly purified by froth flotation using fatty acids as collectors and can be considered as the main representative of the calcium-bearing sparingly-soluble minerals [1,2]. The molecular origins of collector adsorption, intermolecular organization, and hydrophobization at the calcium-bearing minerals-water interface remain poorly resolved. Here, classical molecular dynamics simulations are used to uncover how sodium oleate adsorbs and self-organizes on hydrated fluorite (111) surfaces, from a single molecule to a full monolayer coverage. Benchmarking against previous DFT and AIMD results [3,4] confirms the reliability of the atomistic model. At low coverage, oleate binds strongly to surface calcium atoms, with adsorption energies around −266 kJ $mol^{-1}$, a dominant monodentate adsorption mode, and an angle between surface and molecule of 80º, all in line with the literature [5]. As the surface coverage increases, adsorption evolves into a cooperative process in which lateral chain–chain interactions promote the formation of increasingly ordered hydrophobic domains. Near monolayer completion, this competition between surface anchoring and intermolecular self-assembly leads to stable yet heterogeneous adsorption states. Remarkably, the theoretical adsorption thermodynamics show very good agreement with experimental adsorption enthalpies obtained from total organic carbon (TOC) measurements, bridging molecular simulation and experiments. Altogether, the results provide a compelling molecular picture of how collector adsorption and self-assembly control calcium-bearing minerals hydrophobicity, with direct implications for flotation performance and broader significance for interfacial self-organization in mineral processing systems.

**Keywords:**
Flotattion, fatty-acids, self-assembly monolayer, solid-liquid interface




*Evolution of the self-assembly monolayer formation.*

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